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## EUROPEAN PATENT APPLICATION

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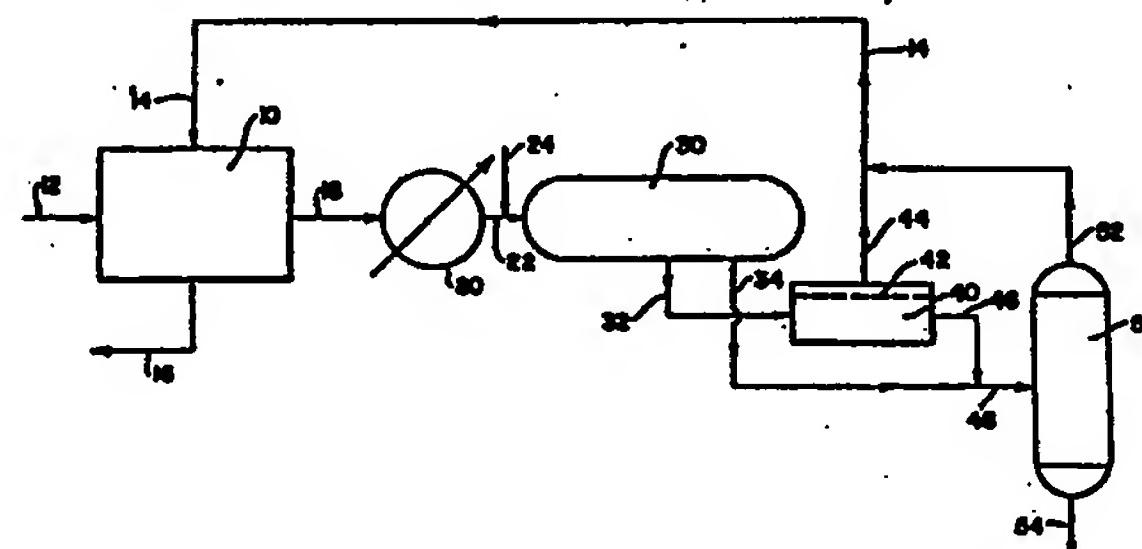
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㉙ Method of separating a mixture by decantation and permeation through a membrane.

㉚ A method for separating a mixture into a first fraction and a second fraction is disclosed. The method comprises passing the mixture (12) into a decantation zone (30) where the solution is separated into a first fraction relatively rich in a first compound and a second fraction relatively deficient in the first compound. One of the separated fractions subsequently is passed (via 32) to a membrane separation zone (40) for further purification. The subject invention is of particular utility in petroleum processing, where the solution passed to the decantation zone may be a petroleum processing fraction, such as filtrate from a dewaxing zone or an extract or raffinate from an extraction separation zone.



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1 BACKGROUND OF THE INVENTION

2           This invention is related to the separation  
3 of a mixture into a first fraction relatively rich in a  
4 first component and a second fraction relatively rich  
5 in a second component. More specifically, this inven-  
6 tion is related to the separation of petroleum pro-  
7 cessing feed streams, especially filtrate, extract or  
8 raffinate streams from dewaxing or extraction zones.

9           In the separation of a mixture, one or more  
10 unit operations may be utilized. Frequently, the par-  
11 ticular unit operation is selected after a consider-  
12 ation of several variables, including the desired  
13 purity of the separated fractions, capital cost of the  
14 equipment, equipment reliability and operating costs.  
15 In the production of lube oils from base feedstock, the  
16 feedstock is processed to remove undesired aromatics  
17 and waxy compounds. Typically, these compounds are  
18 removed by extractive operations in which a solvent  
19 having the desired affinity for one of the feedstock  
20 components is passed concurrently, cross-currently or  
21 countercurrently to the feedstock to effectuate the  
22 separation. For example, in the separation of aromatics  
23 from lube oil feedstock, the feedstock may be contacted  
24 with a solvent such as phenol, furfural, acetone, and  
25 N-methyl pyrrolidone each of which is selectively mis-  
26 cible with the aromatics to be removed. In the sepa-  
27 ration of waxy compounds, the lube oil feedstock fre-  
28 quently is contacted with a solvent or solvent mixture  
29 such as methyl ethyl ketone (MEK) methyl isobutyl  
30 ketone (MIBK), methyl ethyl ketone/toluene, or  
31 acetone/methylene chloride which selectively removes  
32 the waxy compounds. Previously, efforts have been  
33 directed at the subsequent processing of the extract

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1 and raffinate streams from the extraction zone to  
2 separate and recover the solvent, as well as to further  
3 purify the lube oil base, which typically comprises the  
4 raffinate.

5 U.S. Patent No. 2,232,772 is directed at a  
6 dewaxing process in which the solution is chilled and  
7 decanted to separate the filtrate into two liquid  
8 phases for recycle and/or additional processing, such  
9 as by distillation, an energy intensive process.  
10 Additional solvent may be added to the solution to  
11 facilitate the phase separation.

12 U.S. Patent Nos. 3,725,257 and 3,985,644  
13 both are directed at the extractive separation of an  
14 aromaticrich stream from a petroleum fraction. The  
15 extract then is cooled and separated into an aromatic-  
16 rich hydrocarbon phase and a solvent-rich phase. The  
17 solvent-rich phase is recycled either to an inter-  
18 mediate point or to the top of the extractor while the  
19 hydrocarbon-rich phase is passed to a distillation  
20 zone. This process is deficient in that the solvent  
21 returned to the extractor contains significant quan-  
22 tities of aromatic hydrocarbons. Thus, recycling this  
23 recovered solvent to the top of the extractor will  
24 require significantly more solvent for effective  
25 removal of aromatics from the aromatic-containing  
26 feedstock.

27 U.S. Patent No. 2,754,249 also discloses the  
28 extraction of a hydrocarbon fraction to remove non-  
29 paraffinic compounds. The extract is de-oiled by the  
30 addition of a material capable of reducing the solu-  
31 bility of the extracted hydrocarbons in the solvent.  
32 The extract subsequently is decanted, with the layer  
33 containing solvent and anti-solvent distilled to

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1 separate the antisolvent. The solvent, substantially  
2 devoid of antisolvent, then is mixed with solvent  
3 recovered from the raffinate phase and recycled to the  
4 extraction system. This process depends upon the use of  
5 large amounts of anti-solvent to effect the required  
6 separation. Thus, the solvent-rich phase must be dis-  
7 tilled to remove large quantities of anti-solvent,  
8 resulting in this process being energy intensive.

9               U.S. Patent No. 3,556,991 is directed at a  
10 method for removing aromatic hydrocarbons from a  
11 petroleum fraction by solvent extraction. In this  
12 process, the extract is passed through a membrane  
13 separation zone having a membrane permeable to the  
14 aromatic hydrocarbon but not to the solvent. The  
15 retentate solvent then is directed through a distil-  
16 lation zone to further purify the solvent. Although the  
17 membrane separation zone removes a fraction of the  
18 solvent, significant quantities of the solvent must be  
19 removed during the distillation step.

20               Accordingly, it is desirable to provide a  
21 process which is reliable, and offers low operating and  
22 maintenance costs.

23               It is also desirable to provide a process  
24 which requires relatively low capital costs and which  
25 may be retrofitted to existing separation facilities  
26 for improving production rates and/or product quality.

27               The subject invention is directed at the  
28 discovery that decantation and separation of a mixture  
29 prior to passage through a membrane separation zone  
30 improves the flux and/or degree of separation of the  
31 permeate. This procedure thus, may decrease the number

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1 of membrane separation zones required for a given  
2 throughput and/or reduce the load placed on downstream  
3 separation facilities, such as a distillation zone.

4 SUMMARY OF THE INVENTION

5           The subject invention is directed at a  
6 method for separating a mixture comprising a plurality  
7 of compounds into a first fraction relatively rich in a  
8 first compound and a second fraction relatively  
9 deficient in the first compound. The method comprises  
10 the steps of first passing the mixture into a decan-  
11 tation zone wherein the mixture is separated into a  
12 first fraction relatively rich in a first compound and  
13 a second fraction relatively deficient in the first  
14 compound. At least one of the fractions from the  
15 decantation zone then is passed into a membrane  
16 separation zone wherein the fraction is still further  
17 separated into a retentate and a permeate having  
18 unequal concentrations of this first compound.  
19 Depending upon the particular requirements of the  
20 system, the permeate and/or retentate may be recir-  
21 culated to the extraction and/or dewaxing zone, or it  
22 may be further purified as necessary, such as by  
23 passing the permeate and/or retentate into a distil-  
24 lation zone. The subject process is applicable to the  
25 separation of petroleum fractions, particularly the  
26 filtrate, raffinate and/or extract streams from  
27 dewaxing or solvent extraction processes. Depending  
28 upon the specific composition of the solvent used, it  
29 may be advantageous to add an antisolvent to the fil-  
30 trate, extract or raffinate to further assist in the  
31 separation of the streams in the decantation zone.

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1 BRIEF DESCRIPTION OF THE DRAWING

2                 The Figure is a simplified schematic flow  
3 drawing of one method for practicing the subject  
4 invention.

5 DETAILED DESCRIPTION OF THE INVENTION

6                 The subject invention may be of utility in  
7 any process wherein a mixture of two or more compounds  
8 is selectively separated by the use of a semi-permeable  
9 membrane, i.e. a membrane which selectively passes only  
10 certain of the compounds through the membrane. In the  
11 processing of petroleum fractions, particularly lube  
12 oil feedstocks, the aromatics and waxy compounds are  
13 removed utilizing, in part, dewaxing and solvent  
14 extraction techniques well-known in the art.

15                 Referring to the Figure, a conventional  
16 separation zone, such as a solvent dewaxing zone 10 is  
17 shown. A feedstream 12, such as a hydrocarbon feed-  
18 stock, is shown entering dewaxing zone 10 while  
19 recovered solvent is returned to the dewaxing zone  
20 through line 14. Feedstream 12 is separated in dewaxing  
21 zone 10 into a wax cake and a solvent/oil mixture by  
22 filtration or centrifugation. The wax cake is removed  
23 from zone 10 through line 16, while a solvent/oil  
24 stream, generally comprising the filtrate exits  
25 dewaxing zone 10 through line 18. To facilitate phase  
26 separation, the filtrate is cooled prior to and/or  
27 during residence in decantation zone 30. In the present  
28 embodiment, the filtrate stream passes through a heat  
29 removal zone 20, such as a heat exchanger, and exits  
30 through line 22. As described more fully hereinafter,  
31 an anti-solvent optionally may be added to the filtrate  
32 through line 24. The filtrate, with or without anti-

1 solvent, passes into decantation zone 30 where the  
2 filtrate is permitted to separate into two layers. A  
3 first, solvent-rich layer having reduced amounts of the  
4 undesired compounds is removed through line 32, and a  
5 second layer relatively rich in the undesired compounds  
6 and having a reduced concentration of solvent is  
7 removed through line 34. The solvent-rich stream in  
8 line 32 passes into a membrane separation zone 40  
9 having a semi-permeable membrane 42 through which, in  
10 the process shown, a relatively pure solvent stream  
11 passes after which it exits via line 44. The retentate,  
12 with a reduced concentration of solvent, passes through  
13 line 46. In the process shown, streams 34 and 46 are  
14 combined to form stream 48 which passes into a dis-  
15 tillation zone 50. Distillation zone 50 separates  
16 stream 48 into a relatively pure solvent stream 52 and  
17 a relatively concentrated bottoms stream 54 of the  
18 undesired compounds. Solvent streams 52 and 44 are  
19 combined to form stream 14 which is recycled to  
20 dewaxing zone 14 as previously described.

21           Depending upon the desired purity of the  
22 permeate and/or retentate, distillation zone 50 may or  
23 may not be required. In instances where the distilla-  
24 tion zone is the rate limiting operation, the present  
25 invention may permit an increase in the overall pro-  
26 duction rate without adversely affecting the products  
27 from the distillation zone.

28           The following example illustrates the  
29 utility of the subject invention in increasing the flux  
30 through the membrane 42. In this example, the solvent  
31 comprised a mixture of 25 wt.% acetone and 75 wt. %  
32 methylene chloride, which is useful for the solvent  
33 extraction of waxy compounds in a dewaxing operation. A  
34 typical representative filtrate stream was prepared

1 comprising about 20 wt.% hydrocarbon compounds and  
2 about 80 wt.% solvent. This solution was cooled to  
3 about -29°C and allowed to decant for about 5 minutes  
4 into an upper, hydrocarbon-rich layer comprising about  
5 40 vol. % waxy hydrocarbons, and about 60 vol. %  
6 solvent. The lower, solvent-rich layer comprised about  
7 9 vol. % hydrocarbon and about 91 vol. % solvent. The  
8 upper and lower layers each comprised approximately 50  
9 vol. % of the filtrate. The upper layer was removed,  
10 and the lower layer was passed through a membrane  
11 separation zone 40 having a Spectrapore 3500 semi-  
12 permeable membrane using 400 psig pressure. This  
13 membrane, manufactured by Spectrum Medical Industries,  
14 Los Angeles, California, U.S.A. comprised a regenerated  
15 cellulose membrane having a pore size of about 15 Å.  
16 This membrane was preconditioned for use in the subject  
17 process by sequentially permeating the water containing  
18 membrane with methanol and then with methyl ethyl  
19 ketone. The feed solutions contacted the membrane at  
20 400 psig and ambient temperature. As shown in Table I,  
21 removal of the upper hydrocarbon layer enabled the flux  
22 rate to increase substantially while simultaneously  
23 decreasing the oil concentration in the permeate. Such  
24 a system may enable the use of fewer membrane separa-  
25 tion units for a given throughput and/or improve the  
26 quality of the permeate.

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TABLE I

2	Without <u>Decanter</u>	With <u>Decanter</u>
3		
4 Solvent system	25/75 Acetone/MeCl <sub>2</sub>	25/75 Acetone/MeCl <sub>2</sub>
5		
6 Oil Concentration in 7 Extract to Membrane 8 Separation Zone, wt.%	20	7
9 Oil Concentration in 10 Permeate, wt.%	0.9	0.45
11 Flux Rate l/m <sup>2</sup> /day	52	79

12 In actual commercial dewaxing operations it  
 13 is anticipated that membrane separation zone 40 would  
 14 be maintained at a much lower temperature, such as the  
 15 -29°C temperature utilized in the decantation zone 30.  
 16 While the flux rates would be lower at lower temper-  
 17 atures due to the increased viscosity of the permeate,  
 18 the relative flux rate and purity of the permeate still  
 19 would be higher where a decantation zone had been used  
 20 than it would be for a system at comparable operating  
 21 conditions in which the decantation zone had not been  
 22 used.

23 While this example used a pretreated cell-  
 24 ulose membrane, it is clear that other membranes also  
 25 may be suitable. Similarly, while the present example  
 26 was directed at the separation of dewaxed oil from lube  
 27 feedstock, the present invention may be applicable to  
 28 other systems by the use of semi-permeable membranes of  
 29 the appropriate pore size and chemical resistance.

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1                 Depending on the particular characteristics  
2         of the system, it may be desirable to add an anti-  
3         solvent to the stream prior to or during its residence  
4         in decantation zone 30 to improve the separation of the  
5         components between the two layers. To avoid the intro-  
6         duction of additional compounds to the system, the  
7         anti-solvent added frequently comprises that solvent in  
8         the solvent system having the lower solubility for the  
9         compounds to be removed. For example, in dewaxing  
10        solvent systems comprising MEK/MIBK, or MEK/toluene, or  
11        acetone/methylene chloride, the solvent having the  
12        lower solubility for the oil, i.e., MEK or acetone, may  
13        be added as the antisolvent. Also, for example in  
14        extraction, water may be added as the anti-solvent.

15                While Table I has been directed at the  
16         separation of a solvent-lube oil-wax system, it is  
17         clear that the present invention is equally applicable  
18         to other systems in which the compounds present are  
19         separable using a semi-permeable membrane. Similarly,  
20         while the feed to the decantation and/or membrane  
21         separation zone in the present example is filtrate from  
22         a dewaxing process, it is equally clear that the  
23         present invention may be practiced on extract and  
24         raffinate streams from an extraction process. The  
25         present invention also may be applicable to other  
26         separation processes where the feed to the decantation  
27         zone is not an effluent stream from an extraction zone.

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In this patent specification, gauge pressures expressed in pounds per square inch gauge (psig) are converted to their kPa equivalent by multiplication by 6.895.

## CLAIMS:

1               1. A method for separating a first compound  
2 from a mixture comprising a plurality of compounds,  
3 said method characterized by:

4               (a) passing the mixture into a liquid-  
5 liquid decantation zone wherein the mixture is sepa-  
6 rated into a first liquid fraction relatively rich in  
7 the first compound and a second liquid fraction rela-  
8 tively deficient in the first compound; and

9               (b) passing one of the liquid fractions  
10 from the decantation zone into a membrane separation  
11 zone wherein the fraction is still further separated  
12 into a permeate and a retentate having unequal con-  
13 centrations of the first compound.

14              2. The method of claim 1 above further  
15 characterized by the mixture comprising effluent from  
16 an extraction and/or dewaxing zone.

17              3. The method of either claim 1 or claim 2  
18 above further characterized by recirculating       at  
19 least a portion of the second fraction from the  
20 decantation zone to the extraction and/or dewaxing  
21 zone.

22              4. The method of any of claims 1-3 above  
23 further characterized by recirculation of permeate from  
24 the membrane separation zone to the extraction and/or  
25 dewaxing zone.

1           5. The method of any of claims 1-4 above  
2 further characterized by permeate being recirculated  
3 from the membrane separation zone to the extraction  
4 and/or dewaxing zone without further purification.

5           6. The method of any of claims 1-5 above  
6 further characterized by retentate from the membrane  
7 separation zone being passed to a distillate zone for  
8 further separation of a first compound from the mix-  
9 ture.

10          7. The method of any of claims 1-6 further  
11 characterized by the temperature of the mixtures being  
12 reduced prior to and/or during residence of the mixture  
13 in the decantation zone.

14          8. The method of any of claims 1-7 above  
15 further characterized by the addition of an anti-  
16 solvent to the mixture to promote the separation of the  
17 mixture into a first fraction and a second fraction in  
18 the decantation zone.

19          9. The method of any of claims 1-8 above  
20 further characterized by the mixture comprising extract  
21 from an extraction and/or dewaxing zone.

22          10. The method of any of claims 1-9 above  
23 further characterized by the first compound comprising  
24 a hydrocarbon.

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AMENDED  
CLAIMS

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CLAIMS:

1. A method of separating a first compound from the effluent of an extraction and/or dewaxing zone wherein the effluent comprises a mixture of compounds, said method being characterized by:-

5 (a) passing the mixture into a liquid-liquid decantation zone wherein the mixture is separated into a first liquid fraction relatively rich in the first compound and a second liquid fraction relatively deficient in the first compound;

10 (b) passing one of the liquid fractions from the decantation zone into a membrane separation zone wherein the fraction is separated into a permeate and a retentate having unequal concentrations of the first compound; and

15 (c) circulating at least a portion of one fraction from the membrane separation zone to the extraction and/or dewaxing zone.

20 2. The method of claim 1 characterized by re-circulation of permeate from the membrane separation zone to the extraction and/or dewaxing zone.

3. The method of claim 1 or claim 2 characterized by permeate being circulated from the membrane separation zone to the extraction and/or dewaxing zone without further purification.

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**AMENDED**  
**CLAIMS**

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4. The method of any one of claims 1 to 3 characterized by retentate from the membrane separation zone being passed to a distillate zone for further separation of first compound from the mixture.

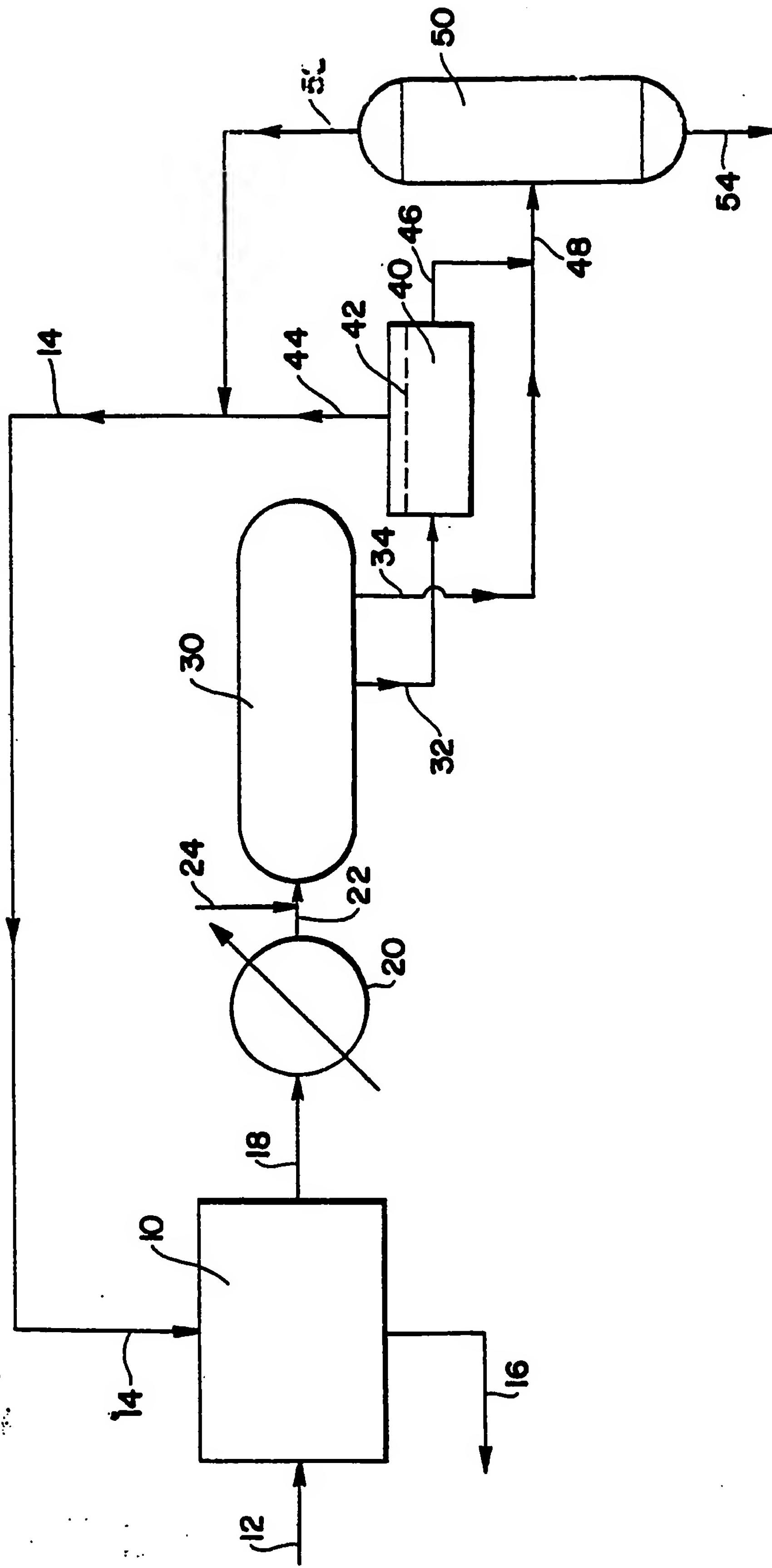
5 5. The method of any one of claims 1 to 4 characterized by the temperature of the mixture being reduced prior to and/or during residence of the mixture in the decantation zone.

10 6. The method of any one of claims 1 to 5 characterized by the addition of an antisolvent to the mixture to promote the separation of the mixture into a first fraction and a second fraction in the decantation zone.

15 7. The method of any one of claims 1 to 6 characterized by the mixture comprising extract from an extraction and/or dewaxing zone.

8. The method of any one of claims 1 to 7 characterized by the first compound comprising a hydrocarbon.

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**EUROPEAN SEARCH REPORT**

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Application number

EP 83 30 7316

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
X	FR-A-2 218 125 (ABCOR INC.) * Figures 1,3; claims 1,8; page 5, lines 3-13 *	1, 6, 10	B 01 D 13/00 B 01 D 17/00 C 10 G 21/28 C 10 G 73/06
Y		2-5, 7-9	
Y	--- EP-A-0 013 834 (EXXON RESEARCH AND ENGIN. CO.) * Figure 3; claims 8,10; page 24, line 23 - page 25, line 21 *	2, 4, 5, 6, 9, 10	
A		1	
Y	--- EP-A-0 043 685 (UNION CARBIDE CORP.) * Abstract; figure 1; claim 1 *	2, 3, 7-10	TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )
A	---	1	B 01 D C 10 G
	---	-/-	
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 01-08-1984	Examiner HOORNAERT P.G.R.J.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
X	<p>TRANSACTIONS A.S.M.E., serie B, JOURNAL OF ENGINEERING FOR INDUSTRY, vol. 98, no. 11, November 1976, pages 1215-1220, New York, US; L.R. HARRIS et al.: "Oily bilge water treatment with a tubular ultrafiltration system" * Page 1215, summary; figure 4; page 1216, column 2, last para- graph - page 1217, column 1, line 20; page 1220, summary of findings *</p> <p>---</p>	1,10	
A	<p>FR-A-2 425 876 (RHONE-POULENC IND.) * Claims 1,5; page 1, lines 16-18; page 3, lines 13-19 *</p> <p>---</p>	1,2,10	
A	<p>EP-A-0 080 684 (ASAHI K.K.K.K.) * Claims 1,16; page 7, lines 23-31; page 22, lines 6-21; page 33, lines 2-20 *</p> <p>-----</p>	1,6,8, 10	TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 01-08-1984	Examiner HOORNAERT P.G.R.J.	
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			